WAVELENGTH CONTROL FOR CAVITY RINGDOWN SPECTROMETER

Inventors: Sze Tan and Bernard Fidric

Field of the Invention

This invention relates to absorption spectroscopy and, in particular, to cavity ring-down spectroscopy (CRDS). In particular, this invention relates to an apparatus and method for controlling the input of laser light into the resonant optical cavity of a CRDS instrument.

Background of the Invention

Cavity Ring-Down Spectroscopy (CRDS) is an increasingly widely used technique for detecting and monitoring analytes, especially when the target analyte is present in very low concentration. Techniques are available which enable the use of CRDS with gaseous, liquid or solid samples. Various aspects of CRDS are described in numerous U.S. Patents such as 5,815,277, 5,903,358, 5,912,740, 6,084,682, 6,094,267, 6,233,052, 6,377,350, 6,452,680, 6,466,322 and 6,532,071. Cavity Ringdown Spectroscopy by K.W Busch and M.A Busch, ACS Symposium Series No 720, 1999 ISBN 0-8412-3600-3, gives a comprehensive, generally up to date overview of many aspects of CRDS technology.

In essence, CRDS involves measuring the decay time of a photon filled, high finesse resonant optical cavity (the ring-down cavity). The cavity is formed by from two to usually three or four ultra-high reflectivity dielectric mirrors, which comprise the optical resonator. Monochromatic light from a laser is injected into the cavity which encloses the analyte sample. The decay time is determined by:

i) the round trip path length of the optical beam within the cavity;

ii) losses inherent in the cavity itself (primarily diffraction losses and losses through the mirrors); and

iii) most importantly, losses due to the frequency dependent losses due to absorption by the target analyte.

Since losses i) and ii) are independent of the analyte, the analyte spectrum is determined by the frequency dependent decay time of the resonant cavity with the target analyte present.

A major advantage of CRDS relative to conventional absorption spectroscopy is that it does not depend on a power-ratio measurement but rather provides an absolute measurement (i.e, decay time).

As above-indicated, cavity ring-down spectroscopy involves measuring the absorption of radiation by a sample via the effects of this absorption on the decay rate (the "ring-down time constant") of an optical cavity. The absorption is measured as a function of the wavelength of light resonating in the cavity to obtain the desired spectrum and/or concentration of a target analyte.

The optical cavity is initially filled with radiation from a laser, and ring-downs are initiated by interrupting this incoming radiation. It is important for the purposes of high-resolution spectroscopy that the wavelength of the laser be precisely known at the time each ring-down occurs. In the present invention the cavity length is adjusted so that (a mode of) the cavity is in resonance with the laser radiation at the time of ring-down. Due to the resonance condition, the intra-cavity intensity builds up rapidly while the laser is on. The accuracy to which the ring-down time constant can be measured improves with increasing intra-cavity optical intensity, so it is desirable to make this quantity (the "cavity filling") as large as possible.

Several factors limit how much cavity filling can be achieved in practice. Due to the very high finesse (or very narrow line width) of the cavity, small fluctuations in the laser wavelength (or the cavity length) can cause the incident light to go into and out of resonance with the cavity. When this happens, the intra-cavity intensity may decrease or fluctuate irregularly while the laser remains turned on. In addition, filling uniformity also affects the repetition rate and hence measurement speed. It is therefore doubly important for the laser to have minimal frequency jitter. For a semiconductor laser, the wavelength is a very sensitive function of both the pump current to, and the temperature of, the laser, making the control of these quantities very important. In particular, achieving good cavity filling at each of a collection of wavelengths (as required for a spectral scan) requires a very low-noise current source and the ability to control the laser pump current over a moderately wide bandwidth (of the order of the inverse cavity lifetime) to maintain the laser output at the desired wavelength set point while the cavity fills up.

A conventional two-mirror, continuous wave (CW) CRDS instrument (200) is shown in Figure 1.

As shown in Fig. 1, light is generated from a narrow band, tunable, continuous wave diode laser 202. Laser 202 is temperature tuned by a temperature controller (not shown) to emit its radiation at a wavelength approximately equal to a desired spectral line of the analyte. An acousto-optic modulator (AOM) 204 is positioned in front of the radiation emitted from laser 202. AOM 204 provides a means for providing light 206 from laser 202 along the optical axis 219 of resonant cavity 218. Light 206 exits AOM 204 and is directed by mirrors 208 and 210 to cavity mirror 220 as light 206a which travels along optical axis 219 and exponentially decays between cavity mirrors 220 and 222 when light 206 is extinguished or deflected from the cavity axis . The measure of this decay is indicative of the presence or lack thereof of a trace species. Detector 212 is coupled between the output of optical cavity 218 and controller 214. Controller 214 is coupled to laser 202, processor 216, and AOM 204. Processor 216 processes signals from optical detector 212 in order to determine the level of trace species in optical resonator 218.

In AOM 204, a pressure transducer (not shown) creates a sound wave that modulates the index of refraction in an active nonlinear crystal (not shown), through a photoelastic effect. The sound wave produces a Bragg diffraction grating that disperses incoming light into multiple orders, predominantly zero order and first order. Different orders have different light beam energy and follow different beam directions. In CW-CRDS,

typically, a first order light beam 206 is aligned along with optical axis 219 of cavity 218 incident on the cavity in-coupling mirror 220, and a zero order beam 224 is idled with a different optical path (higher order beams are very weak and thus not addressed). Thus, AOM 204 controls the direction of beams 206 and 224.

When AOM 204 is on, most light power (typically, up to 80%, depending on size of the beam, crystals used in AOM 204, alignment, etc.) goes to the first order along optical axis 219 as light 206. The remaining beam power goes to the zero order (light 224), or higher orders. The first order beam 206 is used for the input coupling light source; the zero order beam 224 can be used for diagnostic components. Once sufficient light energy is built up within the cavity. AOM 204 is turned off. This results in all the beam power going to the zero order as light 224, and no light 206 is coupled into resonant cavity 218. The light energy inside the cavity then follows an exponential decay (i.e., "rings down").

In order to "turn off" the laser light to optical cavity 218, and thus allow for energy within optical cavity 218 to ring down, AOM 204, under the control of controller 214, redirects (deflects) light from laser 204 along path 224 and thus away from optical path 206 into optical resonator 218.

Some art workers have endeavored to provide an alternative to using an AOM to turn off the transmission of photons into the optical cavity. For example, the system described in WIPO applications 03/098173 (US 2003/0210398) is reported to function as follows:

i) a controller deactivates (shuts off) the laser light source when the light emitted from the cavity reaches a predetermined threshold. The laser is turned off by shunting the laser current away from the laser;

ii) the laser remains shut off for a fixed period significantly exceeding the ring-down time and the cavity rings-down during the initial portion of the fixed shut-off period and the concentration of the target analyte is thereby measured;

iii) the light source is turned back on at the end of this first shut-off period to thereby initiate a second fixed period during which the restarted laser "stabilizes". By setting the laser temperature to an appropriate value, by the end of this period the laser emission frequency should be stabilized at a value which is approximately correct for a given target analyte. The current to the laser is then modulated to more finely vary the laser emission frequency until it coincides with a cavity resonance mode at some point during the modulation resulting in energy build-up within the fixed length cavity. While this system may sometimes have advantages over a system using an AOM to turn off the light into the optical cavity, it is not capable of achieving the degree of precision achievable with an optimized CRDS instrument in accordance with the present invention.

Since the laser emission wavelength depends both on temperature and pump current, adjusting the laser temperature to a preset value so as to provide a nominal (in reality only approximately correct) wavelength, and subsequently modulating the current, can

cause the actual laser wavelength to differ significantly from the desired value. It is not possible to do high-resolution spectroscopy with such a configuration. Equally significant, in this method no mechanism to compensate for the effects of laser aging. It is well known in the laser art that over time the temperature and current required to achieve a particular emission wavelength will change. The above design does not provide a feedback mechanism to detect or compensate for the effects of aging so that over time the instrument will tend to drift away from the analyte absorption feature which it is trying to detect.

Summary of the Invention

In the system of the present invention, both the temperature of and current to the laser are continuously monitored and adjusted to bring the laser emission to the desired wavelength to within a frequency accuracy of approximately 10MHz (0.0003 cm^{-1}). An additional wavelength monitor unit is required for this purpose, and this is used in conjunction with a hardware control loop, which adjusts the laser current. With the help of this control loop, the time to stabilize the laser wavelength is only a few hundred microseconds, as compared to the at least 100ms required by the above-described prior art systems.

An object of the present invention is to provide an improved control system for CW Cavity Ring-Down Spectrometers. In particular, the present invention is directed to an

apparatus and method for precisely controlling the wave length of the light used to illuminate the resonant cavity of a CRDS instrument.

A Cavity ring-down spectrometer includes the following components:

i) the resonant optical cavity which comprises at least two, and preferably three or four, high reflectivity mirrors;

ii) an electrically pumped, semiconductor laser which may, for example, be an external-cavity diode laser (ECDL) or preferably a distributed feedback (DFB) diode laser. The laser provides the light (radiation) which is emitted into the resonant cavity. The wavelength of the radiation produced by the gain medium is dependent on both the temperature of the gain medium and the current pumped into it. For purposes of spectroscopy it is necessary to provide means to tune, i.e., alter the wavelength of the light emitted by the gain medium into the optical cavity to be close to a wavelength absorbed by a target analyte species or to scan over a specific absorption feature. Alternatively, a DBR (Distributed Bragg Reflector) laser can be utilized. Alternatively, an array of DFB or DBR lasers on a single chip, with the lasers of the array having contiguous tuning ranges, can be utilized to provide a broadly tunable system. In such a case the system which controls the laser emission wavelength as hereinafter described, will first select from the array a particular DFB of a desired emission wavelength.

iii) means for turning off (deactivating) the optical signal into the resonant cavity when the laser is at the desired wavelength and the cavity contains photons in a quantity above a threshold level. The threshold is basically determined by the inherent signal to noise ratio of the particular instrument, i.e., the higher the ratio the lower the threshold, i.e., the number of photons in the cavity, required to obtain good spectroscopic results. "Turning off" the light into the cavity permits it to "ring-down". After the cavity has "rung-down" light from the laser is again directed into the optical cavity to fill it up to the threshold level, the optical signal is again turned off and the ring-down process repeated. The distinctive spectrum for any given analyte results from performing the ring-down process over a more or less broad range of wavelengths.

As already indicated, there are a number of conventionally used methods for deactivating the optical signal into the resonant optical cavity in order to permit the cavity to ring-down:

i) change the beam path so that it no longer is aimed at the cavity input mirror;

ii) periodically turn off the current to the laser;

iii) periodically shunting the current to an alternative medium preferably one having electrical properties (e.g., resistance, capacitance and/or inductance) similar to the gain medium;

iv) frequency shift the laser emission out of the resonance range of the cavity by varying the laser input current.

Normally, in methods i) and iv) the laser remains on at all times. The first method conventionally utilizes an acousto-optic modulator (AOM), as previously described. One approach which utilizes the second method is described in previously mentioned published US Application 2003/0210398. In methods ii) and iii) the current flow to the gain medium is turned off (terminated) thereby temporarily deactivating the optical signal.

The present invention is directed to a CRDS instrument and method which sequentially activates (turns on) and shuts off (deactivates) the light into the resonant optical cavity using any one of methods ii) through iv), above. However, the method and apparatus of the present invention differs significantly and advantageously from any of the prior art methods and apparatus, including that described in the afore-mentioned published application.

The method of the present invention includes the following steps:

i) directing a continuous wave optical signal, preferably from a semi-conductor diode laser, into a resonant optical cavity comprising at least two high reflectivity mirrors;

ii) using a first detector to monitor the radiation emitted from the optical cavity through one of these mirrors and determine when the intensity of the emitted radiation is equal to a pre-determined threshold value. Suitable detectors

include, for example, photodiodes, avalanche photodiodes and photo-multiplier tubes. The power of the radiation impinging on the detector is equal to the power of the radiation circulating in the resonant cavity multiplied by the power transmission coefficient of the output mirror. The threshold must be sufficient to provide an adequate signal to noise ratio and thereby provide an accurate determination of the ring-down decay constant (normally referred to as τ).

iii)

using a first controller to deactivate the laser by turning off or shunting the current, thereby interrupting the current flow to the gain medium to thereby permit the cavity to ring-down.

iv)

reactivate the laser by again passing current into the gain medium and thereby cause it to again direct an optical signal into the optical cavity. Note that in this arrangement the laser is alternately on and off, but when on is always positioned to direct its optical beam into the cavity and the emission wavelength is being continuously monitored by a second controller to provide active feedback which enables precise control of the laser emission wavelength.

As an alternative to steps iii) and iv) the optical signal can be deactivated by frequency shifting the laser emission frequency out of the resonance range of the optical cavity or

by use of a beam redirecting AOM as previously described. Reactivation is achieved by returning the input current to a value which brings the laser output back into the resonance range of the cavity. In this alternative embodiment the laser is always “on”.

When a DFB or other semiconductor laser is maintained at constant temperature and the pump current is raised from zero to a constant value, the wavelength of the laser changes rapidly (over up to a few tenths of a nm) before approaching its steady-state value on a timescale of a about a few milliseconds, which limits data acquisition rates. We have found that by using a feedback circuit to vary the laser current, while simultaneously monitoring the laser wavelength, it becomes possible to significantly reduce the time required to obtain a desired wavelength having the stability needed for efficient cavity filling. This significantly reduced the response time of the CRDS instrument. Suitable laser wavelength monitoring can be effected by the use of an etalon in either transmission or reflection, a linear transmission filter or a combination of the foregoing.

In consideration of the above, a cavity ring-down spectrometer in accordance with the present invention performs the following steps.

In a preferred procedure, two look-up tables are constructed, one to record the approximate (coarse value) gain medium temperature and a second to record the current required for the laser to produce a particular desired emission wavelength in the steady state. When using a laser array, such a “look-up table” is made for each laser in the array. In contrast to the prior art, in our design, because the laser emission wavelength is

substantially continuously monitored, the look-up table can be continuously updated during the laser's service life to ensure that the instrument emits at the desired wavelength notwithstanding any changes in the laser itself as a result of aging effects.

At the beginning of each ring-down cycle, the laser is turned on (methods ii) and iii), its emission frequency returned to a value within the resonance range of the cavity i.e., method iv) , or the beam path realigned to the cavity (method i) with the temperature and current being set to the tabulated coarse values to approximately achieve a desired wavelength. At this time an error signal processor which forms part of the second controller is in the reset state, and produces zero output. The output control (which determines input current to the laser diode) for the pump current source is adjusted to the pre-tabulated coarse value. The error signal processor then commences to function in its normal operating state. The input to the processor is the wavelength error signal, which is obtained by noting the difference between the desired wavelength and the laser output as measured by a wavelength monitor (a second detector). A suitable wavelength monitor comprises an etalon, beam splitter and pair of photodiodes. The output from the processor provides a fine correction adjustment to the input current to the laser diode from the current source which reduces the wavelength error to a very low value (e.g., ~10MHz). Prior art control methods do not achieve this precise level of wavelength control. The output of the processor is preferably the sum of a first quantity proportional to the error signal and a second quantity proportional to the integral of the input signal, the output of the processor preferably being limited to ensure that the current to the laser cannot be changed too far from the tabulated value. The wavelength monitor determines when wavelength stabilization has occurred. With our system the time required to

stabilize the laser wavelength at a desired value is only a few hundred microseconds as compared to prior art designs which may require as much as 100 milliseconds. Prior art designs apparently use a fixed length cavity and set the laser temperature to an approximately correct value for the desired wavelength. The current to the laser is then modulated until the laser emits at a wavelength that fortuitously corresponds to a cavity mode. This method does not permit sufficiently precise control of the ring-down wavelength to achieve many of the more demanding and difficult analyses. In addition, the resolution capability of prior art systems is limited by the cavity free spectral range. Since the cavity length will change slightly with a change in temperature, and can randomly change up or down by one-half the free spectral range, this can adversely affect the precision of the system.

In our design, to record ring-downs, the beam path length of the cavity is continuously swept (modulated) over a range of lengths, including that at which the cavity will be in resonance with the incoming light, using, for example, a piezo-electric transducer (PZT) to translate one of the cavity mirrors as described in co-pending, commonly assigned US Patent Application S.N. 10/391,928, filed 3/18/03 the disclosure of which is incorporated herein by this reference. Initially the cavity length controller is in scan mode, and the range of cavity lengths is chosen to be sufficiently large that the round trip length of the cavity changes by at least one wavelength of the optical radiation so that the comb of cavity resonance frequencies will always cover the emitted laser frequency at some point within the sweep. The sweep rate is chosen to be sufficiently slow so that the cavity fills efficiently once resonance is achieved. The cavity round trip length is changed over one

wavelength in approximately 50-200 milliseconds. During the wavelength stabilization period the threshold comparator is turned off to preclude ring-down.

Once the wavelength error is sufficiently small i.e., the wavelength is sufficiently close to the desired wavelength, the cavity intensity detector signal is compared against a preset threshold to determine if there is sufficient light of the desired wavelength in the cavity to initiate a ring-down. This occurs near the time at which the cavity is resonant with the light. As soon as the threshold is reached, the first controller deactivates the optical signal and triggers the data acquisition unit to record the ring-down of the cavity intensity. Determining when the wavelength error is small can be achieved by monitoring the error signal.

After a delay period at least in excess of the ring-down time, and preferably a delay period of about five to ten ring-down times or even greater, which delay period may be either a pre-programmed, fixed time delay (which is preferred), or a delay period determined by noting when the cavity has rung-down by measuring the residual optical intensity in the cavity using the first detector, a new cycle begins by current again being sent to the laser to turn it on once again (or the laser again being caused to direct light into the cavity, as previously described).

In a typical spectroscopic measurement, several ring-downs are recorded with the laser set to the same wavelength, so that the statistical error in the ring-down time may be reduced. Instead of sweeping the cavity length over a wide range of lengths (a full scan)

after the first ring-down has been detected, the range of lengths swept over is reduced so that less time is required for the resonance condition to be satisfied after the laser emission wavelength has stabilized. The means used to control the cavity length is said to be in tracking mode, and the rate of measuring ring-down times is increased preferably to several hundred sweeps per second. For small changes in the laser wavelength, the limits of the range of cavity lengths may be adjusted dynamically so that the cavity tracks the laser. When a larger change in laser wavelength occurs, it is necessary to return the cavity length controller to scan mode so that the cavity resonance may be found again.